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(54) PROCEDE D'EXTRACTION D'ACIDE (METH)ACRYLIQUE
(54) METHOD FOR EXTRACTING (METH)ACRYLIC ACID

(57)
The invention relates to a method for extracting an aqueous solution containing (meth)acrylic acid. Said solution is brought into contact with a solution containing at least one extracting agent which can be converted into (meth)acrylic acid and forms a miscibility gap with the aqueous solution to produce an organic phase containing (meth)acrylic acid and extraction agent and an aqueous phase.

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(54) **PROCEDE D'EXTRACTION D'ACIDE (METH)ACRYLIQUE**
(54) **METHOD FOR EXTRACTING (METH)ACRYLIC ACID**

(57) Procédé d'extraction d'une solution aqueuse qui contient de l'acide (méth)acrylique, par mise en contact avec une solution qui contient au moins un agent d'extraction qui peut être converti en acide (méth)acrylique et qui forme avec la solution aqueuse une lacune de miscibilité, ce qui permet d'obtenir une phase organique qui contient l'acide (méth)acrylique et l'agent d'extraction, ainsi qu'une phase aqueuse.

(57) The invention relates to a method for extracting an aqueous solution containing (meth)acrylic acid. Said solution is brought into contact with a solution containing at least one extracting agent which can be converted into (meth)acrylic acid and forms a miscibility gap with the aqueous solution to produce an organic phase containing (meth)acrylic acid and extraction agent and an aqueous phase.

methacrolein, steam, inert diluent gas (eg. nitrogen) and byproducts (eg. oxides of carbon), lower aldehydes, eg. formaldehyde, high boilers, eg. citraconic acid, and in particular acetic acid, from which the methacrylic acid must subsequently be isolated (cf. for example EP-A 253 409 and DE-A 19 62 431). However, other possible starting compounds are those from which the actual C_4 starting compound, eg. methacrolein, is formed initially as an intermediate during the gas-phase oxidation. An example is the methyl ether of tert-butanol (MTBE).

For the preparation of methacrolein, it is also possible to subject formaldehyde and propionaldehyde to a condensation reaction and to obtain methacrolein by subsequent distillation. Such a process is described in EP-B 58 927. The methacrolein thus obtained can then be converted into methacrylic acid in the conventional manner by catalytic gas-phase oxidation. A reaction of this type is described, inter alia, in EP-B 297 445.

Acrylic acid can be obtained in a similar manner starting from the corresponding C_3 compounds, in particular propene and/or acrolein.

If it is intended to isolate (meth)acrylic acid from the resulting reaction gas mixture by extraction, the reaction gas mixture is first subjected to a condensation stage and then extracted. Thus, EP-B 345 083 describes such a process which comprises a methacrylic acid extraction stage in which methacrylic acid is extracted with a saturated hydrocarbon of 6 to 9 carbon atoms.

According to EP-A 710 643, in a process for the purification of methacrylic acid, an aqueous methacrylic acid solution obtained by cooling and condensing the reaction gas is extracted from the aqueous solution by adding an organic solvent, preferably an aliphatic hydrocarbon of 5 to 9 carbon atoms, an aromatic hydrocarbon, an ester or a mixture thereof.

Japanese Patent JP 57 095 938 describes the extraction of acrylic acid from a dilute

aqueous solution by extraction by means of an oxygen-containing solvent and a tertiary amine. Examples are trioctylamine and 2,6-dimethyl-4-heptanol.

However, all these processes are disadvantageous in that the extraction of (meth)acrylic acid is effected in each case using an assistant which on the one hand is not obtainable without additional costs, and moreover, in such a process, additional steps are required in order to separate off this assistant again, entailing additional costs and additional energy consumption.

None of the prior art processes describes the possibility of extracting (meth)acrylic acid by means of an assistant-free solution. The extracting agents used to date are merely assistants which cannot be converted into (meth)acrylic acid.

Thus, it is an object of the present invention to provide a process for extracting an aqueous solution which contains (meth)acrylic acid, which process can be carried out without assistants and furthermore can be effected using conventional apparatuses and with comparatively low energy consumption.

We have found that this object is achieved by the process according to the invention.

The present invention accordingly relates to a process for extracting an aqueous solution which contains (meth)acrylic acid by bringing it into contact with a solution which contains at least one extracting agent which can be converted into (meth)acrylic acid and forms a miscibility gap with the aqueous solution, wherein an organic phase, which contains (meth)acrylic acid and extracting agent, and an aqueous phase are obtained.

As defined in, inter alia, the claims, the term extracting agent includes all substances which can be converted into (meth)acrylic acid in one or more stages and at the same time forms a miscibility gap with the aqueous solution which contains (meth)acrylic acid.

Particular examples are alkanes, alkanols, alkenes or alkenals of 3 or 4 carbon atoms or mixtures of two or more thereof which can be converted into (meth)acrylic acid and form a miscibility gap with the aqueous solution defined above.

Substances suitable for this purpose are preferably (meth)acrolein, isobutene, propene, propane, butane, isobutyraldehyde, the methyl ether of tert-butanol (MTBE) or a mixture of two or more thereof. (Meth)acrolein is particularly preferably used.

The solution which contains at least one extracting agent which can be converted into (meth)acrylic acid either consists completely of this extracting agent or contains it as a mixture with other substances, eg. water and/or acetic acid. The solution may also contain impurities arising from the preparation process of the components and therefore need not be purified before the extraction.

Additives which improve the extraction effect may also be added to this solution. Examples are antifoams, for example tallow fatty alcohol and other polyalcohols, demulsifiers, such as alkali metal chlorides, and surfactants and substances which extend the miscibility gap, for example higher alkanes, in particular those of 4 to 14 carbon atoms.

There are in principle no restrictions with regard to the concentration of the extracting agent which is contained in this solution and can be converted into (meth)acrylic acid, but the concentration of this extracting agent in the solution is preferably from about 50 to 100, particularly preferably from about 70 to about 99.9, in particular from about 90 to about 97, % by weight.

The solution defined above must in any case have a miscibility gap with the aqueous solution which contains (meth)acrylic acid.

Particularly if the novel process is integrated in a process for the preparation of (meth)acrylic acid or is operated in combination with such a process, it is preferable, if the solution which is used for extracting (meth)acrylic acid and contains at least one extracting agent which can be converted into (meth)acrylic acid is a solution which can be used as a starting material for the (meth)acrylic acid synthesis and preferably has a concentration of from 50 to 100% by weight of extracting agent. It is particularly preferably a solution which contains (meth)acrolein.

The reaction gas mixture which is obtained by oxidation of the C_3/C_4 compounds in the first stage and still contains starting material may, after condensation of said mixture, also be used as the solution which contains at least one extracting agent which can be converted into (meth)acrylic acid, for extracting (meth)acrylic acid.

The extracting agent which is contained in the solution and is present to a certain extent in the aqueous phase after the extraction is preferably recovered by a thermal separation method, for example by stripping with steam or an inert gas, eg. nitrogen, air, carbon dioxide, exit gas from the (meth)acrylic acid preparation or a mixture of two or more thereof, or by recovery by distillation. The extracting agent is transferred virtually completely to the gas phase and can then be used for the preparation of (meth)acrylic acid, if necessary after passing through further (working up) stages.

There are likewise no restrictions at all with regard to the concentration of the (meth)acrylic acid in the aqueous solution. The content of (meth)acrylic acid in this solution is preferably from about 0.01 to about 80, particularly preferably from about 1 to about 40, in particular from about 5 to about 20, % by weight. In addition to (meth)acrylic acid and water, this solution, particularly if it is obtained industrially from the preparation of (meth)acrylic acid, may contain a small amount, as a rule less than about 3% by weight, of the starting material used for the preparation of (meth)acrylic acid and a small amount, as a rule less than 10% by weight, of acetic acid.

As stated above, an organic phase which contains (meth)acrylic acid and extracting agent is obtained in the extraction. The extraction is preferably carried out in such a way that the total amount or virtually the total amount of the (meth)acrylic acid used is present in this phase. In addition to (meth)acrylic acid, the organic phase contains extracting agent and also small amounts of water, acetic acid and high boilers. The resulting aqueous phase may also contain small amounts of (meth)acrylic acid, extracting agent and acetic acid, which however can be removed for the predominant part by thermal separation methods.

According to a preferred embodiment of the novel process, the organic phase which contains (meth)acrylic acid and extracting agent is subjected to a thermal separation method, for example stripping with steam or with an inert gas, eg. nitrogen, air, carbon dioxide, an exit gas formed in the oxidation of the starting materials for the preparation of (meth)acrylic acid or a mixture of these inert gases, or to distillation of the extracting agent/water mixture. In this process, on the one hand, the (meth)acrylic acid, together with the high boilers and the acetic acid, is separated from the predominant part of the extracting agent and water.

There are no particular restrictions at all with regard to the temperature at which the novel process can be carried out. The only precondition is that, at the chosen temperature and the chosen pressure, it is possible for two phases, an organic and an aqueous phase, to form. In general, the novel process is carried out at from about 0 to about 150°C, preferably from about 30 to about 80°C, in particular from about 50 to about 70°C, temperatures above about 68°C being employed at superatmospheric pressure when (meth)acrolein is used as the extracting agent. If other extracting agents are used, temperature and/or pressure must be modified depending on the extracting agent.

All apparatuses which are used in general for extraction, as are described, for example, in Ullmanns Encyklopädie der technischen Chemie, 4th Edition, Vol. 2, page 546 et seq., in particular page 560 et seq. (1972), may be used for carrying out the novel process. Particular examples are mixer-settler apparatuses, packed extraction columns, spray tower extraction columns, pulsed and unpulsed tray columns and packed columns and stirred extraction columns or extraction apparatuses which utilize centrifugal forces.

The aqueous solution which contains (meth)acrylic acid and the solution which contains at least one extracting agent which can be converted into (meth)acrylic acid can be brought into contact with one another either cocurrent, crosscurrent or countercurrent, the extraction by countercurrent being preferred.

The extraction can be carried out in one or more stages, and it is also possible to use combinations of extraction apparatuses.

The process according to the invention can be carried out continuously or batchwise, the continuous procedure being preferred.

It is also possible to carry out the novel extraction process as part of a process for the preparation of (meth)acrylic acid. The amount of (meth)acrylic acid to be extracted corresponds as a rule to the amount of (meth)acrylic acid which was not condensed in the condensation of the reaction mixture obtained directly in the preparation of (meth)acrylic acid by gas-phase oxidation.

As stated above, the extracting agent used for the extraction is preferably recovered after passing through the extraction. Particularly suitable methods for recovering that

part of the extracting agent which is dissolved in the aqueous phase are thermal separation methods, for example stripping with steam or with an inert gas, e.g. nitrogen, air, carbon dioxide, an exit gas formed in the oxidation of the starting materials for the preparation of (meth)acrylic acid or a mixture of these inert gases, or distillation of the extracting agent/water mixture.

The stripping process is generally carried out at temperatures from about 30 to about 100°C, preferably from about 50 to about 80°C, and at a pressure from about 1 to about 1.5 x 10^5 Pa. For other pressures, the temperatures must be accordingly modified.

The type of stripping apparatus used is not subject to any particular restriction, and any conventional stripping apparatuses which permit gas-liquid contact may be used, for example packed towers, sieve-tray towers, bubble cap towers or spray towers. Further readily usable spray apparatuses are described under the keyword absorption column in EP-A 706 986, in column 3, lines 11 to 38, and in the prior art cited therein, which is hereby fully incorporated by reference in the present Application.

As stated above, the (meth)acrylic acid contained in the organic phase is likewise recovered by a thermal separation method, preferably by subjecting the organic phase to a stage for the condensation of (meth)acrylic acid. This stage gives the condensate which contains the main amount of the (meth)acrylic acid present in the organic phase and the main amount of acetic acid, while the extracting agent generally contained in the organic phase is converted into the gaseous state.

For this purpose, the organic phase is fed to a thermal separation method which is operated at a temperature at which the above object, namely the separation of the main amount of (meth)acrylic acid from the main amount of extracting agent, is achieved.

Such separation methods are known from the prior art and are described, for example, inter alia in German Laid-Open Applications DOS 4,235,321 and DOS 3,721,865, for the condensation of the gaseous reaction mixture obtained in the preparation of (meth)acrylic acid.

To avoid or reduce the tendency of (meth)acrylic acid and/or extracting agent to polymerize, a stabilizer, for example phenothiazine, hydroquinone or a derivative

thereof, may also be added to the solutions used in the present process.

As is evident from the above, the problem of the azeotropic (meth)acrylic acid/water mixture can be overcome in a simple manner by means of the novel process by adding extracting agents which can be converted into (meth)acrylic acid. This dispenses with expensive, energy-intensive separation steps involving distillation. Furthermore, contamination problems due to working up the assistant are avoided.

The Examples which follow illustrate the present invention.

EXAMPLES

Example 1

An aqueous solution containing 10.3% by weight of methacrylic acid and 2.2% by weight of acetic acid was extracted with an aqueous methacrolein-containing solution with a methacrolein content of 92% by weight by the countercurrent method in a three-stage mixer-settler cascade which was operated at 50°C. A residence time of 3 minutes was sufficient for phase separation.

The organic phase obtained contained the total amount of the methacrylic acid introduced, the concentration thereof in said phase being 17.6% by weight. 361 g of methacrylic acid were extracted.

Example 2

630 g of aqueous solution containing 10.3% by weight of methacrylic acid and 2.2% by weight of acetic acid were extracted in one stage with 300 g of an organic methacrolein solution. The methacrolein solution contained 7% by weight of water. 580 g

of aqueous phase containing 1.7% by weight of methacrylic acid and 1.2% by weight of acetic acid were obtained.

In the extraction step, the methacrolein solution was laden with 14.4% by weight of methacrylic acid and 1.1% by weight of acetic acid.

Example 3

449 g of aqueous solution containing 1.7% by weight of methacrylic acid and 1.2% by weight of acetic acid were extracted in one stage with 212 g of an organic methacrolein solution. The methacrolein solution contained 7% by weight of water 434 g of aqueous phase containing 0.37% by weight of methacrylic acid and 1.2% by weight of acetic acid were obtained.

In the extraction step, the methacrolein solution was laden with 2.9% by weight of methacrylic acid and 0.73% by weight of acetic acid.

Example 4

328 g of aqueous solution containing 0.37% by weight of methacrylic acid and 1.2% by weight of acetic acid were extracted in one stage with 156 g of an organic methacrolein solution. The methacrolein solution contained 7% by weight of water. 325 g of aqueous phase containing 0.06% by weight of methacrylic acid and 0.68% by weight of acetic acid were obtained.

In the extraction step, the methacrolein solution was laden with 0.65% by weight of methacrylic acid and 0.56% by weight of acetic acid.

Example 5

3.49 kg/h of a first aqueous solution containing 10.3% by weight of methacrylic acid and 2.2% by weight of acetic acid were extracted by the countercurrent method in a three-stage mixer-settler system with 1.63 kg/h of a first methacrolein solution which was introduced into the 3rd settler. The first methacrolein solution contained 7% by weight of water. The first aqueous solution was brought into contact, in the

first extraction stage (first settler) with a third methacrolein solution flowing out of a second settler.

The second aqueous solution flowing out of the first settler was brought into contact with a second methacrolein solution flowing out of a third settler. The third aqueous solution flowing out of the second settler was brought into contact in the third stage with the first methacrolein solution.

3 kg/h of a fourth aqueous phase were obtained from the third settler. This fourth aqueous solution contained 0.8% by weight of methacrylic acid and 1.5% by weight of acetic acid. 2 kg/h of the fourth methacrolein solution were obtained from the first settler. This fourth methacrolein solution contained 17.6% by weight of methacrolein and 1.6% by weight of acetic acid.

The phase separation between the aqueous solutions and the methacrolein solutions was complete after less than 3 minutes in all Examples.

All exemplary experiments were carried out at a temperature of 50°C and at atmospheric pressure.

Patent claims

1. A process for extracting (meth)acrylic acid from an aqueous solution which contains (meth)acrylic acid, comprising:

   bringing the aqueous solution into contact with a solution which

   a) contains at least one extracting agent selected from the group consisting of alkanes, alkanoles, alkenes or alkenals of 3 or 4 carbon atoms and the methyl ether of tert-butanol (MTBE) which can be converted into (meth)-acrylic acid,

   b) forms a miscibility gap with the aqueous solution, and

   c) can be used as starting material for the preparation of (meth)acrylic acid,

   wherein an organic phase, which contains (meth)acrylic acid and extracting agent, and an aqueous phase are obtained.

2. A process as claimed in claim 1, wherein the solution contains the one or more extracting agent, which can be converted into (meth)acrylic acid, in a concentration from 50 to 100% by weight.

3. A process as claimed in claim 1 or 2, wherein the one or more extracting agents which can be converted into (meth)acrylic acid are (meth)acrolein, isobutene, propene, propane, butane, isobutyraldehyde, the methyl ether of tert-butanol (MTBE) or a mixture of two or more thereof.

4. A process as claimed in any of the preceding claims, wherein the aqueous solution which contains (meth)acrylic acid contains the latter in a concentration

of from 0.01 to 80% by weight.

5. A process as claimed in any of the preceding claims, wherein the extraction is carried out in a mixer-settler apparatus, a packed extraction column, a spray tower extraction column, a pulsed or unpulsed tray column or packed column, a stirred extraction column or an extraction apparatus which utilizes centrifugal forces.

6. A process as claimed in any of the preceding claims, wherein the extraction is carried out continuously.

7. A process as claimed in any of the preceding claims, wherein the extraction is carried out countercurrent.

8. A process as claimed in any of the preceding claims, wherein the aqueous phase is subjected to a thermal separation method, an extracting agent-containing gas and a wastewater being obtained.

9. A process as claimed in any of the preceding claims, wherein the organic phase which contains (meth)acrylic acid and extracting agent is subjected to a thermal separation method, a liquid phase which contains (meth)acrylic acid and a gaseous phase which contains extracting agent being obtained.